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Travis

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[54] **PROCESS FOR DEVELOPING PHOTOGRAPHIC ELEMENTS**

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[52] **U.S. Cl.** ..... **96/55,** 96/27 R, 96/50 R, 96/66 R, 96/66.3, 96/100, G03c/1/40

[58] **Field of Search** ..... 96/48 R, 50 R, 66, 96/66.3, 27, 29 D, 100, 55

[56] **References Cited**

UNITED STATES PATENTS

3,701,660 10/1972 Pratt et al. ..... 96/48 R

FOREIGN PATENTS OR APPLICATIONS

239,875 11/1925 Great Britain

777,635 6/1957 Great Britain

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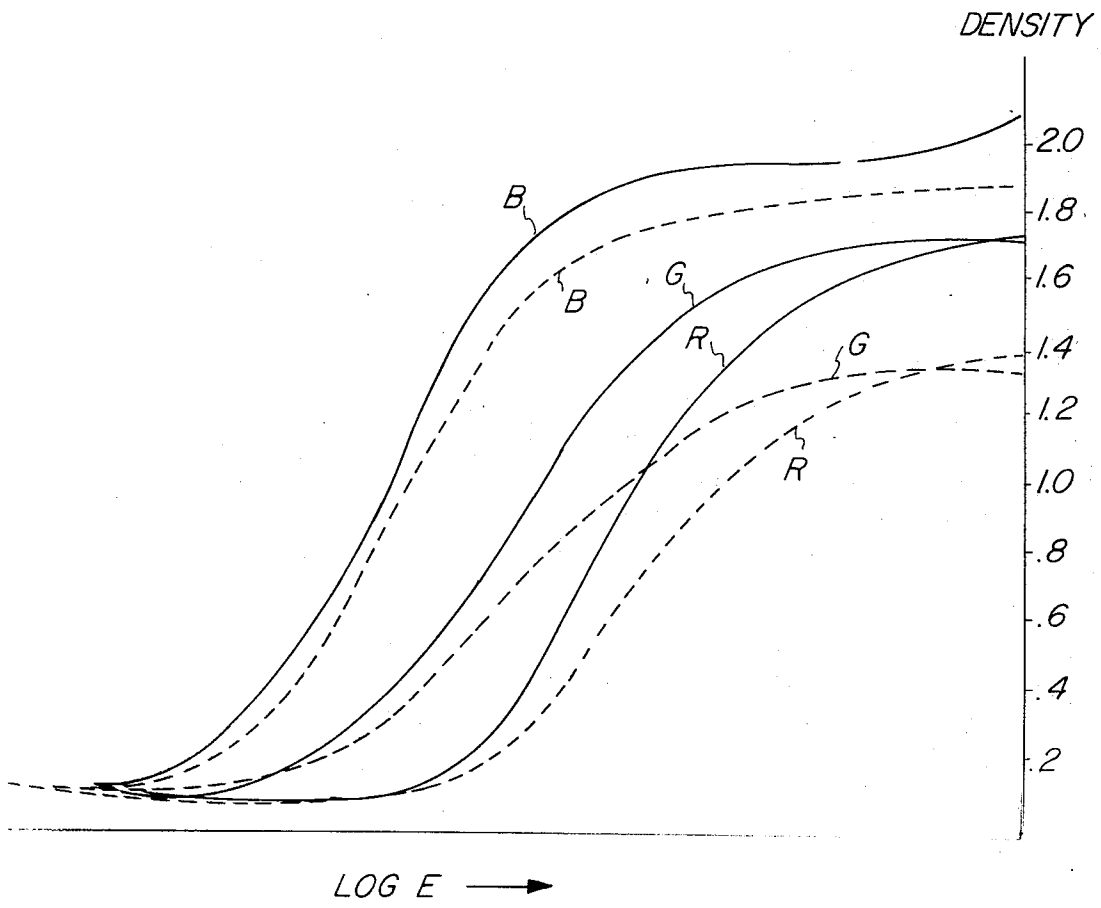
Assistant Examiner—Richard L. Schilling
Attorney—Robert W. Hampton et al.

[57] **ABSTRACT**

Improved processes are disclosed for providing an image record in a photographic element which comprises a support and at least one layer thereon containing a silver halide emulsion which has associated therewith an image dye-providing color coupler. Generally, the process comprises the improvement wherein a photographic element containing a silver halide and an imagewise distribution of metallic silver is contacted in the presence of a color-developing agent with an amplifier composition which contains a cobalt (III) complex.

40 Claims, 4 Drawing Figures



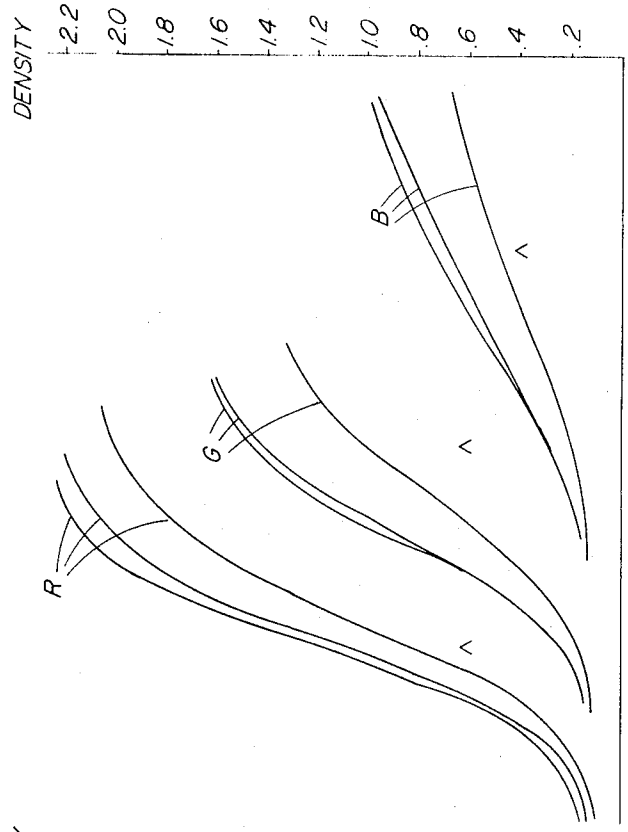

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FIG. 2

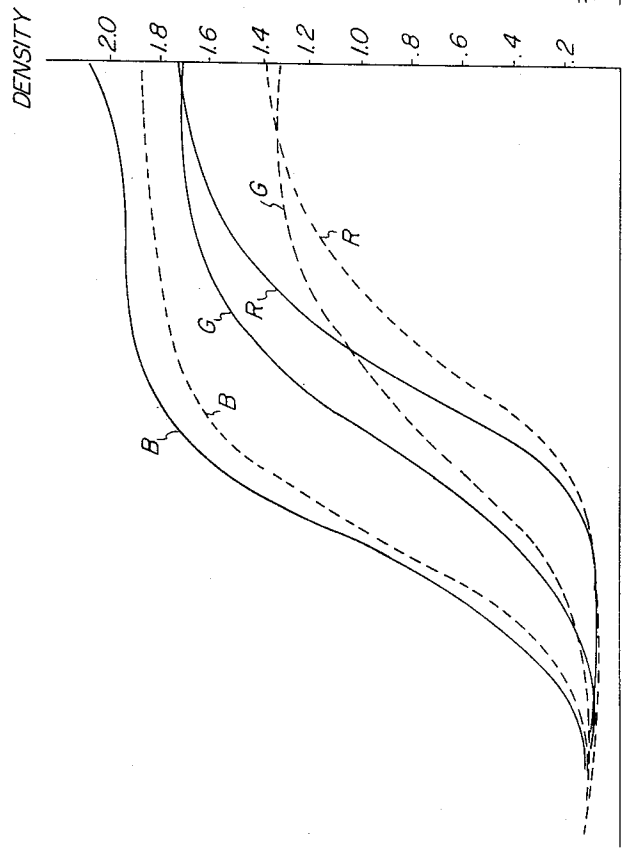
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FIG. 1

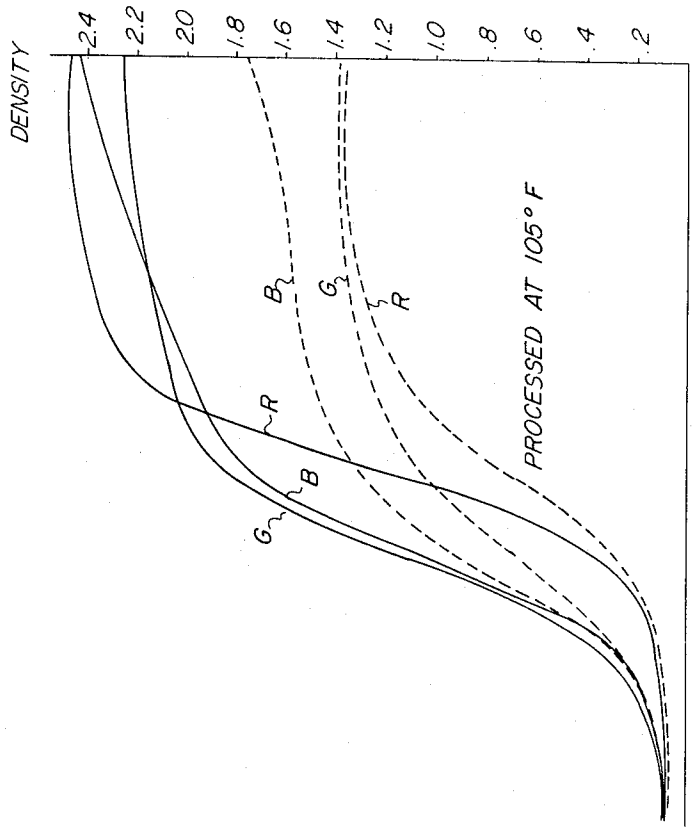
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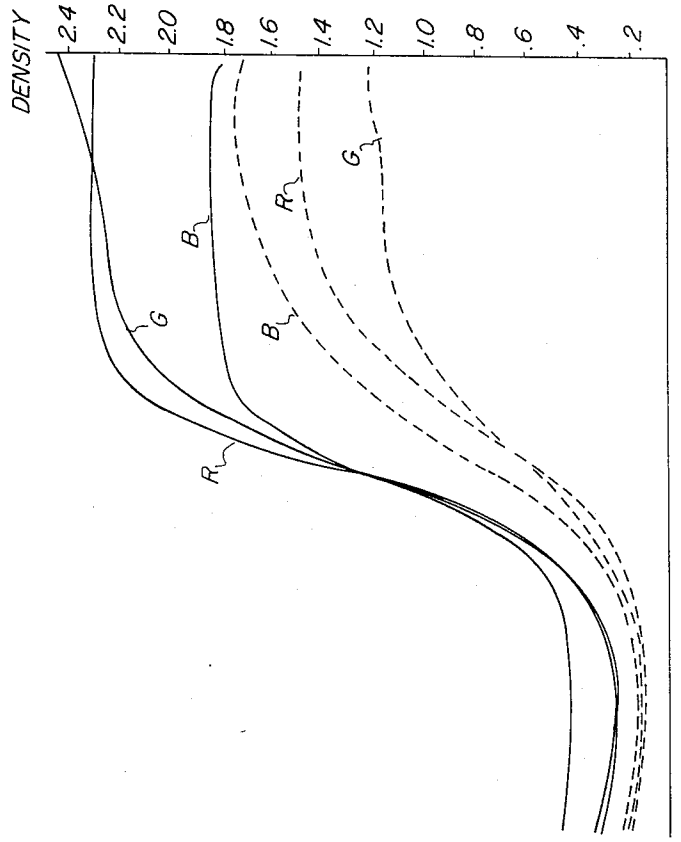
FIG. 4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R
B
R
G
LOG E

FIG. 3

PROCESS FOR DEVELOPING PHOTOGRAPHIC ELEMENTS

This invention relates to a process for developing photographic elements which comprise layer units containing imagewise-exposed silver halide having associated therewith a photographic color coupler. In one aspect, this invention relates to a process for developing a visible image record in photographic elements which comprise color-providing layer units containing a low silver coverage. In another aspect, this invention relates to a continuous process for developing imagewise-exposed photographic elements which comprise at least two color-providing layer units wherein, if desired, at least a portion of the image dye can be produced under roomlight conditions.

It is known in the art to process photographic elements comprising silver halide emulsions and photographic color couplers wherein said element is contacted with an aromatic primary amino silver halide developing agent to form silver and dye. Other references such as U.S. Pat. Nos. 2,750,292 by Dippel et al issued June 12, 1956, and U.S. Pat. No. 2,173,739 by Weber issued Sept. 19, 1939, disclose processes for intensifying an image formed by a light-sensitive metal salt by treating the imagewise-exposed element with a color-developing agent and a photographic color coupler in the presence of developable silver halide or with a physical developing agent to form an image dye in the areas of development. More recently, British Patent 1,268,126 also disclosed a process of intensifying a silver image by treating a developed silver image with solutions containing peroxy compounds and color developers.

However, several of the methods available in the art do not appear to be practical on a commercial basis due to several problems inherent in the system, including instability of the solutions used to intensify the image record recorded by the light-sensitive metal salt. Where the silver is bleached and redevelopment takes place with a color developer and a coupler, the bleaching step is quite critical as the latent image can be lost where bleaching has completely converted a silver grain to silver halide and, moreover, solutions containing both color-developing agent and color coupler are prone to formation of dye in the bath through aerial oxidation of the developer, etc., causing dye contamination, and also these systems are generally limited to one-color systems. Where a physical developing agent is used in combination with a color coupler and a color-developing agent, the processing baths are often autocatalytic since the reaction products of the redox reaction with the physical developer provide a catalyst for more redox reactions.

New processes for developing and amplifying an image record recorded in a light-sensitive metal salt are disclosed in Bissonette, U.S. Ser. No. 189,289, entitled "Image-Forming Processes and Compositions" filed Oct. 14, 1971, and incorporated herein by reference. In one embodiment, the process disclosed relates to image formation in photographic elements comprising color-providing layer units containing a silver halide emulsion having associated therewith a color coupler. In the process, the photographic element is contacted with a photographic color-developing agent and a metal complex, such as a cobalt(III) complex having a coordination number of 6, until the desired dye density

is obtained. The cobalt complex is apparently reduced to cobalt (II), which is not a catalyst for further redox reaction, in the presence of silver, and the color developer is oxidized whereby it can react with the color coupler in each respective layer unit to form the desired image dye. Certain preferred photographic elements which can be processed by this procedure are described in Bissonette, U.S. Ser. No. 256,072, entitled "Photographic Elements" filed on even date herewith and incorporated herein by reference.

I have now found an improved procedure for processing photographic elements which comprise a support and at least one layer thereon containing a silver halide emulsion which has associated therewith an image dye-providing color coupler. Generally, this process comprises the improvement in forming a visible image record in a photographic element wherein the photographic element comprising both silver halide and an imagewise distribution of metallic silver (i.e., a photographic element which has not been fixed to remove the undeveloped silver halide) is contacted in the presence of a color-developing agent with an amplifier composition which represses substantially additional net silver development and which contains a cobalt (III) complex having a coordination number of 6, wherein said contact is maintained under conditions which reduce cobalt(III) to cobalt(II) and in turn oxidize said color-developing agent, whereby image dye is formed from the color coupler in said photographic element and said oxidized color-developing agent. The metallic silver in the photographic element can be latent image silver and is preferably metallic silver formed in a reaction with a silver halide reducing agent such as by development of a latent image with a silver halide developer. While latent image silver can be used as a catalyst in the amplification, dye production can generally be expedited by providing larger catalytic surfaces as produced in silver halide development. The color-developing agent can be present in the amplification bath but is preferably imbibed into the element prior to contact with the amplifier composition. In certain embodiments, the metallic silver is provided, when larger than latent image quantities are desired, in a bath which contains a color-developing agent, such as an aromatic primary amino compound, which can reduce silver halide to silver and in turn produce image dye through its reaction products. In certain preferred embodiments, metallic silver is produced, before amplification, in a bath in the presence of a black-and-white developing agent and a color-developing agent wherein improved results with respect to shortened process time and matched developability of the various layers in a multilayer photographic element can be obtained.

In one highly preferred embodiment, this invention relates to an improved process of producing image dye in an imagewise-exposed photographic element having a support and at least one layer thereon containing a silver halide emulsion having associated therewith an image dye-providing color coupler wherein said process comprises 1) development of said imagewise-exposed photographic element with a silver halide developing agent to produce an imagewise distribution of metallic silver and imbibition of a color-developing agent in said photographic element and then 2) contacting said photographic element which contains silver halide and said imagewise distribution of metallic silver with an amplifier composition which represses substan-

tially additional net silver development, wherein said amplifier composition contains a cobalt(III) metal complex having a coordination number of 6 and said amplifier composition is maintained in contact with said photographic element under conditions which reduce cobalt(III) to cobalt(II), which in turn oxidizes said color-developing agent whereby additional image dye is provided from said image dye-providing color coupler and said oxidized color-developing agent.

The elements processed, as above, can, of course, be bleached, fixed and washed, etc., in the normal manner after contact with the amplifier. Generally, the improved processes of this invention reduce the necessity of fixing the silver halide out of a photographic element before amplification and also reduce the problems associated with silver halide development in an amplifier bath wherein the amount of catalytic silver formation may be very dependent on conditions, reaction by-products, etc. Generally, this process also provides highly improved stability of development compositions and amplifying compositions and is especially suited to continuous processing of color photographic elements. The process is especially advantageous in processing multicolor photographic elements since stability in processing solutions is highly improved allowing reproducible results over long periods of operating time.

In one preferred embodiment, the amplifier solution contains a sufficient quantity of a development restrainer or combination of development restrainers to repress substantially any further net silver development.

In another embodiment, the color-developing agent is an aromatic primary amino compound and is preferably a phenylenediamine color-developing agent.

In another preferred embodiment where high rates of processing are desired, the photographic element is developed in an aqueous bath and contacted with an amplifying solution which is maintained at temperatures above 90° F. and preferably above 100° F. The process of this invention enables one to achieve low wet times in processing since the baths are relatively stable at high temperatures.

In another preferred embodiment, the photographic element is developed in a liquid which is substantially free of a cobalt(III) metal complex having a coordination number of 6.

In another preferred embodiment, the amplifier solution is substantially free of silver halide solvents or contains less than 30 percent, by weight, of the amount of silver halide solvent which would be necessary to fix the silver halide emulsion in the element being processed.

In another embodiment, the photographic elements processed in accordance with this invention preferably contain a water-insoluble image dye-providing color coupler dissolved in a coupler solvent.

In still another embodiment, the photographic element is processed in a bath containing a coupling accelerator which is an alcohol and the amplifier solution preferably contains a coupling accelerator which is an alcohol.

In a highly preferred embodiment, this invention relates to an improved procedure for processing a multicolor photographic element comprising at least two color-providing layer units which each contains a silver halide emulsion and an image dye-providing color coupler in at least a 40 percent and preferably a 70 percent stoichiometric excess based on effective silver coverage in said layer. When the photographic element of this embodiment is a three-color element, the red and green recording layers are preferably in accordance with said color-providing layer units above, and the blue recording layer can be coated in accordance with said definition, but where it is necessary to obtain differential photographic speed between the blue recording layer and other recording layers, it may be desirable to use high coverages of silver and different ratios of coupler to silver in the blue-sensitive layer.

In still another highly preferred embodiment, the photographic elements of this invention comprise at least one and preferably two image dye-providing layer units wherein the silver halide is coated at a coverage of less than 30 mg. of silver per ft.^{2}.

In a highly preferred embodiment, a development restrainer is used in the amplifier bath in sufficient quantities to repress substantially further development of silver halide. Improved fog levels can be obtained if development is not allowed to proceed in the amplification bath, especially in continuous processes where one may encounter ammonia buildup in the amplifier.

In one embodiment, the preferred development restrainers are water-soluble bromide compounds such as KBr, etc., or heterocyclic compounds such as tetrazoles, azaindines and triazoles which are free of mercapto or ionic iodide groups. Development restrainers as a class of compounds are known in the art, as mentioned in U.S. Pat. No. 3,458,317 issued July 19, 1969. Development restrainers which have ionic iodide groups or mercapto groups appear to retard the catalytic effect of silver. Typical preferred development restrainers include high levels of KBr such as 2 to 40 g./l., methyl benzotriazole, benzotriazole, 3-methyl-1,3-benzothiazolium bromide, 5-nitrobenzimidazole, decamethylene bis(benzothiazolium bromide), and the like. Other useful organic development restrainers include the sodium salt of 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, the sodium salt of 4-hydroxy-6-methyl-2-methylmercapto-1,3,3a,7-tetrazaindene, 4,5-dihydro-1,4-diphenyl-3,5-phenylamino-1,2,4-triazole and the like. The heterocyclic development restrainers are generally incorporated in the amplifier at concentrations of 0.01 to 2.0 g./l. In certain embodiments, the heterocyclic groups containing sulfur substitution can be used as development restrainers where the compound as used in the amplifier remains in its thione form rather than in the thiole or mercapto form. In highly preferred embodiments, a combination of an alkali metal bromide and an organic development restrainer are present in the amplifier composition.

The amplifying baths of this invention preferably contain only low amounts or are substantialy free of silver halide solvents. If high amounts of solvents are present, there is very little noticeable amplification effect in the bath. Therefore, the amplifying baths generally comprise less than 30 percent by weight of the amount of a silver halide solvent which would be necessary to fix a silver halide emulsion. The fixing processes are well-known in the art, for example, as disclosed in Stephen, U.S. Pat. No. 3,615,508 issued Oct. 26, 1971.

As used herein, the terms "photographic color coupler" and "image dye-providing color coupler" include any compound which reacts (or couples) with the oxidation products of primary aromatic amino developing agent on photographic development to form an image

dye, and are nondiffusible in a hydrophilic colloid binder (e.g., gelatin) useful fo photographic silver halide, and also those couplers which provide useful image dyes when reacted with oxidized primary aromatic amino developing agents such as by a coupler-release mechanism. The couplers can form diffusible or nondiffusible dyes. Typical useful color couplers include phenolic 5-pyrazolone and open-chain ketomethylene couplers. Specific cyan, magenta and yellow dye-forming couplers which can be employed in the practice of this invention are described in Graham et al, U.S. Pat. No. 3,046,129 issued Jan. 24, 1962, column 15, line 45, through column 18, line 51, which disclosure is incorporated herein by reference. Such color couplers can be dispersed in any convenient manner, such as by using the solvents and the techniques described by U.S. Pat. No. 2,322,027 by Jelley et al issued June 15, 1943, or U.S. Pat. No. 2,801,171 by Fierke et al issued July 30, 1957. When coupler solvents are employed, the most useful weight ratios of color coupler to coupler solvent range from about 1:3 to 1:0.1. The useful couplers include Fischer-type incorporated couplers such as those described in Fischer, U.S. Pat. No. 1,055,155 issued Mar. 4, 1913, and particularly nondiffusible Fischer-type couplers containing branch carbon chains, e.g., those referred to in the references cited in Frohlich et al, U.S. Pat. No. 2,376,679 issued May 22, 1945, column 2, lines 50–60. Particularly useful in the practice of this invention are the nondiffusible color couplers which form nondiffusible dyes.

In certain preferred embodiments, the incorporated couplers in the layer units of this invention are water-insoluble color couplers which are incorporated in a coupler solvent which is preferably a moderately polar solvent. Typical useful solvents include tri-o-cresyl phosphate, di-n-butyl phthalate, diethyl lauramide, 2,4-diarylphenol, liquid dye stabilizers as described in an article entitled "Improved Photographic Dye Image Stabilizer-Solvent," Product Licensing Index, Vol. 83, March, 1971, and the like. The coupler solvents in the elements appear to aid the imbibition of color developer where it is carried into an amplifier bath via the element.

The photographic elements processed in accordance with this invention generally comprise a light-sensitive silver halide emulsion wherein the halide is generally less than 6 mole percent iodide and preferably less than 3 percent iodide and, in some highly preferred embodiments, is less than 0.25 percent iodide. If iodide is near the surface of the emulsion grains, it can build up in the solutions at a high level during development and amplification and affect dye production in the amplification step. Therefore, high amounts of iodide in the emulsion are generally avoided, especially when the element is to be processed in a continuous-process apparatus.

The term "nondiffusible" used herein as applied to couplers and products derived from couplers has the meaning commonly applied to the term in color photography and denotes materials which for all practical purposes do not migrate or wander through photographic hydrophilic colloid layers, such as gelatin, particularly during processing in aqueous alkaline solutions. The same meaning is attached to the term "immobile." The terms "diffusible" and "mobile" have the converse meaning.

The photographic elements of this invention, as defined above, comprise a support having thereon image dye-providing layer units. A multicolor photographic element comprises at least two of said image dye-providing layer units which each records light primarily in different regions of the light spectrum. The layer unit comprises a light-sensitive silver salt, which is generally spectrally sensitized to a specific region of the light spectrum, and has associated therewith a photographic color coupler. In certain embodiments, the color-providing layer units are effectively isolated from other layer units by barrier layers, spacer layers, layers containing scavengers for oxidized developer and the like to prevent any substantial color contamination between the image dye-providing layer units. The effective isolation of the layer units is known in the art and is utilized to prevent color contamination in many commercial color products.

The photographic elements of this invention preferably comprise a support having thereon at least one image dye-providing layer units and preferably at least two image dye-providing layer units containing a light-sensitive silver salt, preferably silver halide, having associated therewith a stoichiometric excess of coupler of at least 40 percent and at least preferably 70 percent. The equivalency of color couplers is known in the art, for example, the 4 equivalent couplers require 4 moles of oxidized color developer, which in turn requires development of 4 moles of silver, to produce 1 mole of dye. Thus, for a stoichiometric reaction with silver halide one equivalent weight of this coupler will be 0.25 mole. In accordance with this embodiment, the color image-providing unit comprises at least a 40 percent excess of the equivalent weight of image dye-providing color coupler required to react with the silver and preferably a 70 percent excess of said coupler based on effective silver. In certain highly preferred embodiments, the photographic color couplers are employed in the image dye-providing layer units at a concentration of at least three times, such as from three to 20 times, the weight of the silver in the silver halide emulsion, or at a stoichiometric excess of at least 110 percent based on effective silver in said layer unit. Advantageously, the coupler is present in an amount sufficient to give a density of at least 1.7 and preferably at least 2.0 when coated on a paper support and preferably at least 3.0 when coated on a transparent film support. Generally, the coupler is present in said layer units in at least 1×10^{-5} moles/ft.^{2}. Preferably, the difference between the maximum density and the minimum density (which can comprise unbleached silver) is at least 0.6 and preferably at least 1.0. Preferably, the photographic elements prepared in accordance with this invention are those described in Bissonette, U.S. Ser. No. 256,072, entitled "Photographic Elements," filed on even data herewith and incorporated herein by reference.

Advantageously, the photographic color couplers utilized are selected so that they will give a good neutral. Preferably, the cyan dye formed has its major absorption between about 600 and 700 nm., the magenta dye has its major absorption between about 500 and 600 nm., and the yellow dye has its major absorption between about 400 and 500 nm.

Generally, each of the color-providing layer units of the photographic elements contains a light-sensitive silver halide. In one preferred embodiment, the color-providing layer units comprise a silver salt at a concentration of up to 30 mg. of silver per square foot. However, while the silver halide is preferably present at

concentrations based on silver of less than 30 mg./ft.^{2}, it is possible to coat emulsions at higher silver coverages within this embodiment, as long as no more than 30 mg./ft.^{2} of silver develops; for example, such emulsions may contain silver halide grains which are relatively light-insensitive or may contain developer restrainers such as development inhibitor-releasing couplers, and still provide a photographic element which is advantageously used in the various processes as described herein to produce improved image records. In some instances, relatively light-insensitive silver halide grains or development restrainers are desirable to enable one to obtain more uniform coating coverage with less precise coating equipment, as well as for other reasons. Thus, highly preferred photographic elements processed according to this invention contain at least two color-providing layer units, each containing a silver halide emulsion, defined in terms of "effective coverage" and developability, as one which, when it is fully exposed and processed for about 1 minute at 100° F. in Developer A as described in Example 1, will provide less than 30 mg. of metallic silver per ft.^{2} and preferably less than 15 mg./ft.^{2}. It is understood that the term "effective silver" refers to that amount of silver which is produced in this test and that ratios of coupler to silver are based on effective silver which is produced by this type of development when so specified herein. In most instances, the quantity of effective silver as silver halide in the undeveloped, unexposed photographic element will be quite similar to quantity of total silver present as silver halide. The fully exposed layer containing silver halide emulsion is one which is exposed to Dmax as is well-known in the art, for example, by exposue exposure a 500-watt, 3000°K lamp for about 10 seconds (total exposure at the film plane = 11.3×10^4 ergs./cm.^{2}).

The photographic elements processed in accordance with this invention generally can contain negative silver halide emulsions, direct-positive silver halide emulsions, silver halide emulsions designed for processing in reversal processes, and the like. It is understood, of course, that with negative emulsions the catalytic metallic silver development will be in the exposed areas whereas with direct-positive emulsions the catalytic metalic silver will be formed in the unexposed areas.

The amplifiers of this invention comprise a cobalt (III) metal complex. Such complexes feature a molecule having a cobalt atom or ion. This cobalt atom or ion is surrounded by groups of atoms, ions or other molecules which are generically referred to as ligands. The cobalt atom or ion in the center of these complexes is a Lewis acid; the ligands are Lewis bases. Werner complexes are well-known examples of such complexes. The useful cobalt salts are typically capable of existing in at least two valent states. In a preferred aspect of the invention, the cobalt complexes are those referred to by American chemists as "inert" and by European chemists as "robust." Particularly useful are complexes of a cobalt ion with a ligand which, when a test sample thereof is dissolved at 0.1 molar concentration at 20° C. in an inert solvent solution also containing 0.1 molar concentration of a tagged ligand of the same species which is uncoordinated, exhibits essentially no exchange of uncoordinated and coordinated ligands for at least 1 minute, and preferably for at least several hours, such as up to 5 hours or more. This test is advantageously conducted under the pH conditions which will be utilized in the practice of the invention. In silver halide photography, this generally will be a pH of over about 8. Many cobalt metal complexes useful in this invention show essentially no exchange of uncoordinated and coordinated ligands for several days. The definition of inert metal complexes and the method of measuring ligand exchange using radioactive isotopes to tag ligands are well-known in the art; see, for example, Taube, Chem. Rev., Vol. 50, p. 69 (1952) and Basolo and Pearson, Mechanisms of Inorganic Reactions, A Study of Metal Complexes and Solutions, 2nd Edition, 1967, published by John Wiley and Sons, p. 141. Further details on measurement of ligand exchange appear in articles by Adamson et al, J. Am. Chem. Soc., Vol. 73, p. 4789 (1951). The inert metal complexes should be contrasted with labile complexes which, when tested by the method described above, have a reaction half-life generally less than 1 minute. Metal chelates are a special type of metal complex in which the same ligand (or molecule) is attached to the central metal ion at two or more different points. The metal chelates generally exhibit somewhat slower ligand exchange than nonchelated complexes. Labile-type chelates may have a half-life of several seconds, or perhaps slightly longer. Generally, the oxidizing agents employed are not reduced to a zero valent metal during the redox reaction of the invention.

Preferred cobalt complexes in accordance with this process have coordination numbers of 6 and are known as octahedral complexes. Cobalt complexes are especially useful in the practice of this invention.

A wide variety of ligands can be used with a metal ion to form suitable cobalt complexes. Nearly all Lewis bases (i.e., substances having an unshared pair of electrons) can be ligands in cobalt complexes. Some typical useful ligands include the halides, e.g., chloride, bromide, fluoride, nitrite, water, amino, etc., as well as such common ligands as those referred to on page 44 of Basolo et al, supra. The lability of a complex is influenced by the nature of the ligands selected in forming said complex.

Particularly useful cobalt complexes have a coordination number of 6 and have a ligand selected from the group consisting of ethylenediamine(en), propylenediamine(tn), diethylenetriamine(dien), triethylenetetraamine(trien), ammine(NH_3), nitrate, nitrite, azide, chloride, thiocyanate, isothiocyanate, water and carbonate. The preferred cobalt complexes comprise 1) at least two ethylenediamine ligands or 2) at least five amine ligands or 3) one triethylenetetraamine ligand. Especially useful are the cobalt hexammine salts (e.g., the chloride, bromide, sulfite, sulfate, perchlorate, nitrite and acetate salts). Some other specific highly useful cobalt complexes include those having one of the following formulas: $[Co(NH_3)_5H_2O]X$; $[Co(NH_3)_5CO_3]X$; $[Co(NH_3)_5Cl]X$; $[Co(NH_3)_4CO_3]X$; $[Co(en)_3]X$; cis-$[Co(en)_2(N_3)_2]X$; trans-$[Co(en)_2Cl(NCS)]X$; trans-$[Co(en)_2(N_3)_2]X$; cis-$[Co(en)_2(NH_3)N_3]X$; cis-$[Co(en)_2Cl_2]X$; trans-$[Co(en)_2Cl_2]X$; $[Co(en)_2(SCN)_2]X$; $[Co(en)_2(NCS)_2]X$; $[Co(tn)_3]X$; $[Co(tn)_2(en)]X$; and $[Co(tn)(en)_2]X$; wherein X represents one or more anions determined by the charge neutralization rule.

With many complexes, such as cobalt hexammine, the anions selected can substantially effect the reducibility of the complex. The following ions are listed in the order of those which give increasing stability to co-

balt hexammine complexes: bromide, chloride, nitrite, perchlorate, acetate, carbonate, sulfite and sulfate. Other ions will also effect the reducibility of the complex. These ions should, therefore, be chosen to provide complexes exhibiting the desired degree of reducibility. Some other useful anions include chloride, nitrate, thiocyanate, dithionate and hydroxide. Neutral complexes such as $[Co(dien)(SCN)_2OH]$ are useful, but positively charged complexes are generally preferred.

A theory has been advanced to explain the low reactivity between the reducing agent and the central metal atom or ion of the metal complex. It appears that the ligands constitute an effective barrier to reaction between reducing agents and the central metal atom or ion. The barrier may be set up by ligands tightly bound to and surrounding the central metal atom or ion. In the presence of certain catalysts, it seems that one or more of the ligands may be bound less tightly to the central metal atom or ion, thus facilitating reaction between the central metal atom or ion and the reducing agent. However, this invention is not limited to that theory.

Numerous color-developing agents can be imbibed in the photographic element in accordance with the present invention. The color-developing agents utilized herein undergo redox reaction with the oxidizing agent at a catalytic surface. Especially preferred color-developing agents are those which reduce silver halide to metallic silver, such as those which are capable of developing imagewise-exposed light-sensitive photographic silver halide. Typical preferred color-developing agents are aromatic primary amine color-developing agents such as p-aminophenols (which form particularly stable redox combinations with certain complexes, e.g., $[Co(en)_3]Cl_3$) or p-phenylenediamines. Useful color-developing agents include 3-acetamido-4-amino-N,N-diethylaniline, P-amino-N-ethyl-N-β-hydroxyethylaniline sulfate, N,N-diethyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene, N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline, 4-amino-N-ethyl-3-methyl-N-(β-sulfoethyl)aniline, 4-amino-N-butyl-N-γ-sulfobutylaniline, 4-amino-N,N-diethyl-3-n-propylaniline hydrochloride, and the like. See Bent et al, JACS, Vol. 73, pp. 3100–3125 (1951), and Mees and James, The Theory of the Photographic Process, 3rd Edition, 1966, published by MacMillan Co., New York, pp. 278–311, for further typical, useful developing agents. It will be appreciated that many of the subject color-developing agents are most effective at high pH, such as a pH from about 8 to 13.

In one highly preferred embodiment, aromatic primary amino color-developing agents which provide good results in the process of this invention are 4-amino-N,N-diethylaniline hydrochloride, 4-amino-3-methyl-N,N-diethylaniline hydrochloride, 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline sulfate hydrate, 4-amino-3-methyl-N-ethyl-N-β-hydroxyethylaniline sulfate, 4-amino-3-dimethylamino-N,N-diethylaniline sulfate hydrate, 4-amino-3-methoxy-N-ethyl-N-β-hydroxyethylaniline hydrochloride, 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-paratoluene sulfonate, and 4-amino-3-β-(methanesulfonamido)ethyl-N,N-diethylaniline dihydrochloride.

The black-and-white silver halide developers, as referred to herein, generally refer to those developers which do not couple with photographic color couplers to form useful image dyes. The black-and-white silver halide developers can be effectively used in some instances in the formation or development of the metallic silver in the photographic element. Typical useful developers of this type include hydroquinones, catechols, 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-3-pyrazolidone and the like, 1-, d or isoascorbic acid, reductones, N-methyl-p-aminophenols, and the like.

The amplifier bath can generally comprise any liquid as a carrier medium, but the liquid is preferably predominantly water. The bath generally comprises from about 0.2 to about 20 g. per liter of the transition metal ion complex which preferably is maintained at between about 1 to about 15 g./l. However, generally higher concentrations of cobalt complexes can be used in preferred amplifier baths of this invention without adverse sensitometric effects compared with color-developing solutions which contain the cobalt complexes which contain sufficient color-developing agent to develop substantial amounts of silver halide rapidly.

The amplifier bath generally contains a development restrainer and preferably contains enough development restrainer to repress any further silver formation. Thus, the sensitometric changes associated with the development of silver are avoided. Moreover, this feature enables one to use various grain sizes in various layers of a multicolor element to obtain a balanced photographic element and simultaneously provide substantially uniform color formation in each layer, whereby balanced color can be obtained at several densities by inspection.

The organic development restrainers (i.e., other than the inorganic development restrainers such as the alkali metal bromides) mentioned previously can be used in the bath in combination with the inorganic development restrainers or alone, but are preferably used in combination with alkali metal bromides. Generally, the organic development restrainers are used in concentrations of from 0 to 2 g. and preferably from 0.01 to 1 g./l.

The amplifier bath is generally operated in a pH range of from 6 to 14 and preferably at pH ranges of 8 to 12.

The amplifying baths contain only small amounts of or are substantially free of silver halide solvents such as sodium thiosulfate, thiocyanates, thioethers and the like. While bromide ions are often desirable in small amounts of about 2 to 40 g./l. of amplifying solution to repress development, high concentrations such as above 200 g./l. could function to bleach silver halide layers and, likewise, defeat the primary amplification step. In certain embodiments, it is also desirable to maintain the ammonia in the amplifier at less than 10 g./l. since high ammonia concentrations can act as a silver halide solvent, thus allowing bleaching of the silver image.

The term "silver halide solvents" generally refers to compounds and concentration levels of those compounds which, when employed in an aqueous solution (60° C.), are capable of dissolving more than ten times the amount (by weight) of silver chloride than that which can be dissolved by water at 60° C.

The concentration of a solvent necessary to fix a silver halide layer is understood to mean that concentration of solvent in a liquid bath which will remove sub-

stantially all silver bromide from a photographic element containing a single silver bromide gelatin emulsion layer coated at 30 mg. silver per ft.^{2} in 1½ minutes at 105° F. maintained at a pH range within 4.0–12.0.

The amplifier bath is generally maintained under conditions to repress further net metallic silver formation in the photographic element. However, since color developer can be carried into the amplifier bath in certain embodiments by imbibition in the element, buildup of color developer in the bath can occur. Generally, in those embodiments the concentration of color developer in the amplifier solution is maintained below 3 g./l. and preferably below 1 g./l. of amplifier solution. With the higher concentrations of color developer, such as above 0.5 g./l., it is desirable to incorporate an antioxidant in the amplifier bath, such as sulfites and the like. In certain embodiments where exact sensitometric effects are desired throughout the run, the concentration of the color developer is maintained at a constant level. In certain preferred embodiments, color-developer scavengers and the like are used in the bath to keep the amplifier bath substantially free of unoxidized effective color developer.

Generally, with most color developers sufficient unoxidized color developer can be imbibed in the photographic element so that developer exhaustion is not a severe problem in amplification of the dye image. However, the changes in the concentration of the color developer in the amplifier can vary the time required in the amplifier bath since the color developer apparently diffuses out of the element more rapidly when the color-developing agent concentration in the amplifier bath is very low. However, the problem of variations in color-developer concentration is minimal when continuous processes are used, such as continuous web processes.

In one embodiment, the highly preferred organic development restrainers which are useful in the amplifiers of this invention can be further characterized by the following test. Preferred organic development restrainers or combinations of development restrainers with an alkali metal bromide are those which, when incorporated at about 200 mg./l. in a bath of the following composition:

benzyl alcohol	15 ml./l.
K_2SO_3	2 g./l.
$[Co(NH_3)6]Cl_3$	10 g./l.
KBr	0.5 g./l.
K_2CO_3	30 g./l.
Na_4EDTA	5 g./l.
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidene di-p-toluene sulfonate	5 g./l.
water to 1 liter	
pH 10.1 at 75° F.	

will produce a substantially equal or higher Dmax and a substantially equal or lower Dmin than a similar sample processed in the bath without the development restrainer wherein the sample is a photographic element comprising a transparent support and one emulsion layer thereon comprising a silver chlorobromide emulsion at 30 mg. of Ag/ft.^{2} and sufficient color coupler to produce a Dmax of at least 3.0 when reacted on an equal stoichiometric basis with oxidized color developer, such as oxidized 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine-di-paratoluene sulfonate, and said element is first fully exposed to Dmax and developed in a black-and-white developer such as Kodak Developer D–19 for 4 minutes at room temperature and fixed with sodium thiosulfate to remove substantially all undeveloped silver halide.

Several of the organic development restrainers have an additive or superadditiVe effect when used in combination with an alkali metal bromide as shown in some of the following examples.

The amplifier bath can be operated over a wide range of temperatures depending on the effect desired. Generally, the amplifier bath is much more stable than amplifier baths previously used and, therefore, is preferably used in processes where it is operated at temperatures above 90° F. and more preferably above 100° F. to decrease the residence time of a photographic element in the bath, thus speeding up the process. The amplifier baths of this invention which are held for 1 week at 105° F. provide substantially the same development properties as a fresh amplifier bath.

The developing baths and amplifier solutions of this invention preferably contain a coupling accelerator which can be an alcohol including aromatic alcohols such as benzyl alcohol, which appears to increase dye yields. Preferably the alcohol is used in the respective baths at a concentration of up to 40 g./l. and preferably from about 2 g. to 20 g./l. Coupling accelerators are known in the art, for example, the alcohols disclosed in U.S. Pat. No. 2,304,925 by Jelley issued Dec. 15, 1942, U.S. Pat. No. 2,950,920 by Schwan et al issued Aug. 30, 1960, and the like.

The improved processes of this invention can be carried out in several types of processing equipment. Simple manual tray or dip tank processing can be used, as well as processes as described by Tregillus et al, U.S. Pat. No. 3,179,517 issued Apr. 20, 1965, roller transport processes as described in Russell et al, U.S. Pat. No. 3,025,779 issued Mar. 20, 1962, and the like. Preferably, the process is carried out in a unidirectional processing equipment where the element leaves a bath in the same relative direction with respect to the plane of the element as it enters the bath. In certain preferred embodiments, a continuous web of the photographic material is processed in unidirectional continuous-processing equipment.

In still other embodiments, the processing solutions can be used in image transfer processes with the developer and amplifier put in separate rupturable pods, such as in the general format as disclosed in Cole, U.S. Pat. No. 3,635,707 issued Jan. 18, 1972, and the like.

Several features of the present process are apparent from FIGS. 1-4 accompanying this application.

FIG. 1 is an H and D curve of the image records of Example 1.

FIG. 2 is an H and D curve of the image records of Example 3, with the curves for the respective image-recording layers separated for clarity with the caret indicating the point of the 11th step on the 21-stepwedge sensitometric exposure for each set of curves.

FIG. 3 is an H and D curve of the image records of Example 4.

FIG. 4 is an H and D curve of the image records of Example 6. The designations B, G and R refer to the curves produced by the blue-sensitive layer unit, the green-sensitive layer unit and the red-sensitive layer unit respectively.

The invention can be further illustrated by the following examples.

EXAMPLE 1

The improvements in amplifying the image record in the red and green recording layer of a photographic element are readily apparent when processing by first developing the element in a color developer and then inserting the element containing silver halide and an imagewise distribution of metallic silver into an amplifier bath.

A photographic element is prepared by coating the following layers in order on a paper support:

1. a layer containing a blue-sensitive AgClBr emulsion at 16 mg. Ag/ft.², gelatin at 150 mg./ft.² and a 2-equivalent coupler, yellow dye-forming coupler α-pivalyl-α-[4-(4-benzyloxyphenylsulfonyl)phenoxy]-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)butyramido]acetanilide, at 75 mg./ft.² dissolved in di-n-butyl phthalate coupler solvent at 18.75 mg./ft.²;
2. a gelatin interlayer at 80 mg./ft.²;
3. a layer containing a green-sensitive AgClBr emulsion at 10 mg. of Ag/ft.², gelatin at 60 mg./ft.² and a 4-equivalent magenta coupler, magenta dye-forming coupler 1-(2,4,6-trichlorophenyl)-3-{5-[α-(3-tert-butyl-4-hydroxyphenoxy)tetradecaneamido]-2-chloroanilino}-5-pyrazolone, at 25 mg./ft.², dissolved in tri-cresyl phosphate coupler solvent at 12.5 mg./ft.²;
4. a gelatin interlayer containing 231 mg. gelatin/ft.²;
5. a layer containing a red-sensitive AgClBr layer at 6 mg. Ag./ft.², gelatin at 65 mg./ft.² and a 2-equivalent cyan coupler, cyan dye-forming coupler 2-[α-(2,4-ditert-amylphenoxy)butyramido]-4,6-dichloro-5-methylphenol, at 35 mg./ft.², dissolved in di-n-butyl phthalate coupler solvent at 17.5 mg./ft.²;
6. a gelatin overlayer at 80 mg./ft.² of gelatin.

Samples of the coating are sensitometrically exposed to a graduated-density test object and then processed at a temperature of 32° C. in the following sequence:

	Test 1A (Control)	Test 1B
color-develop	3.5 min.	3.5 min.
amplify		1 min.
bleach-fix	1.5 min.	1.5 min.
wash	2 min.	1 min.
stabilize	1 min.	1 min.

The respective baths have the following compositions:

Color Developer A

benzyl alcohol	10 ml.
K_2SO_3	2 g.
KBr	0.4 g.
hydroxylamine sulfate	2 g.
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-paratoluene sulfonate	5 g.
K_2CO_3	30 g.
Na_4EDTA	5 g.
water to 1 liter	
pH 10.1 at 24° C.	

*EDTA means ethylenediaminotetraacetic acid as used herein.

Amplifier

$[Co(NH_3)6]Cl_3$	10 g.
KBr	2 g.
water to 1 liter	

Bleach-Fix

$(NH_4)_2S_2O_3$	92.5 g.
NH4[Fe(EDTA)]	50.6 g.
EDTA	2.9 g.
Na_2SO_3	12.0 g.
water to 1 liter	
pH6.8 at 80° F.	

Stabilizer

citric acid	6.15 g.
acetic acid	13.1 g.
benzoic acid	0.34 g.
KOH	5.97 g.
water to 1 liter	
pH 3.60 at 80° F.	

Test 1A is run at the optimum time of development to produce Dmax with the cyan and magenta dyes. While this amount of developed silver is more than necessary for the amplification process of Test 1B, the development time is held constant to show that the amplification step will generate additional dye beyond that provided in the development step.

The H and D curves of the elements of Tests 1A and 1B are produced in FIG. 1. The density of the dyes produced in the red-, blue- and green-sensitive layers are reported as dashed lines for Test 1A and solid lines for Test 1B.

In the above process, sufficient color developer is carried into the amplifier bath to produce the desired dye density. If additional density is desired, more color developer can be added to the amplifier bath or longer times can be used in the amplifier bath. The KBr in the above amplifier appears to suppress development sufficiently to allow the amplification step to be carried out in roomlight.

EXAMPLE 2

The procedure of Test 1B of Example 1 is repeated with the provision that a 1-minute wash is included between the color development and amplification steps. No significant loss in image density occurs which indicates that this color developer is imbibed into the coating in a sufficient quantity to provide for further dye formation in the amplification bath.

EXAMPLE 3

Additional samples prepared and exposed as described in Example 1 are processed by the procedure of Test 1B, except the development time is 15 seconds and the amplification step is run at 1, 2 and 3 minutes in separate tests.

Separated H and D curves for each layer matched at common threshold speeds are shown in FIG. 2. The results indicate that a dye image can be attained with a limited quantity of initially developed catalytic image silver if the dwell time of the photographic material in the amplifier bath is prolonged. It is also observed in a separate processing run that the combination 2-minute color development/3-minute amplification does not lead to a higher density of image dye than a combination 1-minute color development/3-minute amplification. However, speed and fog increase with prolonged development time.

It is observed that by controlling the time in the amplifier bath, color images of variable contrast and constant threshold speed can now be produced with one and the same reflection print material. Such contrast control is attainable in conventional photographic processes only with great difficulty. This aspect of my invention is in part illustrated in FIG. 2. However, in order to obtain better color balance with the photographic element, it is apparent that longer initial development times are desirable to obtain more silver in the

blue-sensitive layer. This longer development time is demonstrated in the following example.

EXAMPLE 4

The imagewise-exposed element of Example 1 is processed according to procedures below to provide for better developability of the blue-sensitive layer:

	Minutes at 100° F. Test 4A	Test 4B
develop	1	1
amplify	0	3
bleach-fix	1½	1½
wash	2	2
stabilize	1	1

The developer, bleach-fix and stabilization baths are the same as Example 1, and the amplification bath is made as follows:

benzyl alcohol	15 ml./l.
K_2SO_3	2 g./l.
KBr	2 g./l.
$Co(NH_3)_6Cl_3$	10 g./l.
K_2CO_3	30 g./l.
Na_4EDTA	5 g./l.
Water to 1 liter	
pH 10.1 at 75° F.	

The results are shown in FIG. 3 on an H and D curve where the solid lines represent Test 4B and the dashed lines represent the results of Test 4A. The blue-sensitive layer apparently produces more catalytic silver than is shown in Example 3, and as a result provides improved matched dye production in the amplification bath. This amplifier is designed to give high contrast and low sensitivity to build-up effects. This includes carry-over of the color developing solution and subsequent buildup of ammonia in the amplifier. Similar results are obtained with the concentrations of 5-methylbenzotriazole of about 0.3 g./l. The 5-methylbenzotriazole prevents development and fog growth, thus stabilizing the overall process response.

EXAMPLE 5

A repeat of the procedures of Test 4B of Example 4 is made wherein the $[Co(NH_3)_6]Cl_3$ is replaced with equimolar amounts respectively of $[Co(NH_3)_5H_2O]Cl_3$, $[Co(en)_2(dien)]$-Cl_2·HCl, $[Co(NH_3)_5(H_2O)](ClO_4)_3$, $[Co(NO_2)_3(NH_3)_3]$, $[Co(NH_3)_4(CO_3)]NO_3$, trans-$[Co(en)_2(Cl)_2]Cl$·HCl, trans-$[Co(en)_2(N_3)(NO_2)]S_2O_6$, $[Co(trien)(NO_2)_2]NO_3$·H_2O, cis-$[Co(trien)(Cl)_2]Cl$, $[Co(en)_2(N_3)_2]NO_3$, $[Co(en)_2(NO_2)_2](ClO_4)_3$, $[Co(trien)(N_3)_2]NO_2$, $[Co(en)_2(NH_3)_2]Cl_3$, $[Co(tn)_3]Cl_3$, $[Co(tn)_2(en)]Cl_3$ and $[Co(tn)(en)_2]Cl_3$.

With each of the cobalt metal complexes a useful dye image is obtained.

EXAMPLE 6

A photographic element is prepared and imagewise-exposed as described in Example 1 and processed as follows:

	Test 6A at 105° F.	Test 6B at 105° F.	Test 6C at 120° F.
develop	1 min.	1 min.	25 sec.
amplify	2 min.	0 min.	45 sec.
bleach-fix	1 min.	1 min.	30 sec.
wash	1½ min.	1½ min.	45 sec.
Total:	5½ min.		2 min., 25 sec.

The developer is as follows:

benzyl alcohol	15 ml./l.
K_2CO_3	30 g./l.
KBr	0.5 g./l.
K_2SO_3	4.0 g./l.
hydroxylamine sulfate	2 g./l.
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-paratoluene sulfonate	7.5 g./l.
diamino propanol tetraacetic acid	3.0 g./l.
Water to 1 liter	
pH 10.08 at 75° F.	

The amplifier has the following composition:

benzyl alcohol	15 ml./l.
K_2SO_3	2 g./l.
KBr	5 g./l.
$[Co(NH_3)_6]Cl_3$	10 g./l.
K_2CO_3	7.5 g./l.
diamino propanol tetraacetic acid	10 g./l.
5-methylbenzotriazole	0.3 g./l.
Water to 1 liter	
pH 10.1 at 75° F.	

The bleach-fix bath is as follows:

ammonium thiosulfate 60%	150 ml.
Na_2SO_3	15 g./l.
diamino propanol tetraacetic acid	3 g./l.
glacial acetic acid	20 ml./l.
$[Co(NH_3)_6]Cl_3$	3 g./l.
water to 1 liter	
pH 4.5 at 75° F.	

The element processed in Test 6A at 105° F. produces a good image record with a sensitometric H and D curve as shown in FIG. 4. The H and D curve where no amplification is used is shown in FIG. 4 in dashed lines. It is apparent that good matched color production can be obtained by continuing to amplify the catalytic silver in each respective layer. Thus, one can raise the contrast and dye Dmax by controlling development and amplification.

The developing solution and amplifier solution are held at 105° F. for extended periods of time with periodic processing of similar elements. After 7 days there are no significant changes apparent in the records produced in this system.

In the above amplifying bath a combination of an inorganic development restrainer, KBr and an organic development restrainer, 5-methylbenzotriazole, are used to repress additional development and fog. Comparing FIGS. 3 and 4, it is apparent that the fog levels are reduced by the combination of the development restrainers.

The elements processed in Test 6C produce a sensitometric curve very similar to Test 6A, but the total processing time is considerably reduced.

In this example, the bleach-fix bath is preferably maintained with a cobalt metal salt level of about 2 to 6 g./l. This can be achieved by addition or carry-over from the amplifier bath. When 10 g./l. are present in the amplifier bath, enough cobalt salt is apprently apparently into the bleach-fix solution to keep the level at about 3 g./l with most multicolor photographic elements.

EXAMPLE 7

Test 6A is repeated with the photographic element which is prepared and imagewise-exposed as described in Example 1, with the exception that the amplifier bath is used for only 1½ minutes and the $[Co(NH_3)_6]Cl_3$ is replaced, respectively, with equimolar amounts of $[Co(NH_3)_6](C_2H_3O_2)_3$, $[Co(NH_3)_6](NO_3)_3$, $[Co(NH_3)_6]_2(SO_4)_3$, $[Co(NH_3)_5(C_2H_3O_2)](NO_3)_2$ and $[Co(NH_3)_5H_2O](ClO_4)_3$. Good dye images are obtained in each instance

which have much higher density than the control run through Test 6B.

EXAMPLE 8

Test 6A is repeated with a photographic element which is prepared and imagewise-exposed as described in Example 1 with the exception that the amplifier is used for only 1½ minutes and the color-developing agent in the developer is replaced in separate tests, respectively, with 2.5 g./l. of 4-amino-3-methyl-N,N-diethylaniline hydrochloride, 5.0 g./l. of 4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline sulfate hydrate, and 5.0 g./l. of 4-amino-N-ethyl-N-β-hydroxyethylaniline sulfate. The maximum dye densities obtained are substantially the same as those obtained with the color-developing agent utilized in Test 6A when the amplification step is run for 1½ minute.

EXAMPLE 9

A photographic element prepared and imagewise-exposed as described in Example 1 is processed in a continuous process as follows:

developer	1 min.
amplifier	1½ min.
bleach-fix	1 min.
wash	1½ min.

The amplifier, bleach-fix and wash are the same as in Example 6. The developer is varied in each test to the constituency as follows:

	Test A	Test B	Test C	Test D
benzyl alcohol	15 g./l.	same	same	same
K_2CO_3	30 g./l.	same	same	same
KBr	0.5 g./l.	same	same	same
hydroxylamine sulfate	2.0 g./l.	same	same	same
diamino propanol tetraacetic acid	3.0 g./l.	same	same	same
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonate	2.5 g./l.	7.5 g./l.	5.0 g./l.	2.5 g./l.
1-phenyl-4,4-dimethyl-3-pyrazolidone	0	0	25 mg./l.	100 mg./l.
Water to 1 liter				

The element developed in Test A with low amounts of color developer produces low yellow dye density but a cyan density of 2.3 and a magenta density of about 1.9. Tests B, C and D all produce dye densities in the element of yellow, cyan and magenta of about 2.0–2.4. Thus, as more black-and-white developer is added to the developing solution, the concentration of the color-developing agent can be reduced and high dye densities can still be achieved in the amplification bath.

The use of lower concentrations of color developer in the developer bath aids in preventing buildup of the color-developing agent in the amplifier bath, thus alleviating problems associated with any buildup of color developer.

EXAMPLE 10

A photographic film element is prepared as follows (with all ingredients as listed in mg./ft.²):

1. cellulose acetate support;
2. a layer containing a blue-sensitive silver bromoiodide emulsion (1.14% iodide) at 61 mg. of Ag (1.0 micron grain), the yellow coupler α-pivalyl-α-(4-carboxyphenoxy)-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)butyramido]acetanilide at 132 mg. dissolved 1:1 in tricresyl phosphate, and gelatin at 253 mg.;
3. layer containing gelatin at 43 mg.;
4. layer containing a red-sensitive silver chlorobromide (80/20) emulsion (0.25 micron grain size) at 10 mg. of silver, a cyan coupler 2-[α-(2,4-di-tert-amylphenoxy)butyramido]-4,6-dichloro-5-methylphenol at 79 mg. dissolved 1:3 in di-n-butyl phthalate, and gelatin at 207 mg.;
5. layer containing gelatin at 43 mg.
6. layer containing green-sensitive silver chlorobromide (80/20) emulsion (0.25 micron grain size) at 20 mg., magenta coupler 1-(2,4-dimethyl-6-chlorophenyl-3-]α-(3-n-pentadecylphenoxy)-butyramido]-5-pyrazolone at 139 mg. dissolved 1:1 in di-n-butyl phthalate, and gelatin at 162 mg.;
7. layer containing gelatin at 68 mg.

Samples of the film element are exposed on a sensitometer and processed as follows:

	Test 10A (105° F.)	Test 10B (105° F.)
develop	1 min.	1 min.
amplify	0	2 min.
bleach-fix	1½ min.	1½ min.
wash	1½ min.	1½ min.

The developer has the composition:

Na_4EDTA	4 g./l.
K_2CO_3	40 g./l.
KBr	2 g./l.
K_2SO_3	4 g./l.
4-amino-3-methyl-N,N-diethylaniline hydrochloride	3.0 g./l.
water to 1 liter	
pH 10.65 at 75° F.	

The amplifier has the composition:

K_2SO_3	2.0 g./l.
KBr	5 g./l.
$[Co(NH_3)_6]Cl_3$	10 g./l.
diaminopropanol tetraacetic acid	5 g./l.
5-methylbenzotriazole	0.5 g./l.
K_2CO_3	20.0 g./l.
water to 1 liter	
pH 10.65 at 75° F.	

The bleach-fix bath is as described in Example 6.

The densities for the samples processed in Tests 10A and 10B are as follows:

	Test 10A (control)		Test 10B	
	Dmin	Dmax	Dmin	Dmax
yellow	0.15	1.7	0.15	above 3.7
cyan	0.15	1.46	0.15	above 3.2
magenta	0.15	1.64	0.15	above 3.7

It is apparent that photographic film elements having low silver coverages can be processed to provide good image records where cyan, yellow and magenta dyes have high densities in the Dmax areas.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A process of providing or intensifying a visible image record in an imagewise-exposed photographic element which comprises at least one color-providing layer unit which contains silver halide and an imagewise distribution of metallic silver having associated therewith an image dye-providing photographic color coupler, said process comprising contacting said photographic element in the presence of a color-developing agent with an amplifier composition which contains 1) a development restrainer in a concentration sufficient

to repress substantially additional net silver development and 2) a cobalt (III) complex having a coordination number of 6, wherein said contact is maintained under conditions which reduce cobalt (III) to cobalt-(II) and in turn oxidize said color-developing agent whereby image dye is formed from the color coupler in said layer unit and the oxidized color-developing agent in the areas corresponding to the imagewise distribution of metallic silver.

2. A process according to claim **1** wherein said color-developing agent is an aromatic primary amino compound.

3. A process according to claim **1** wherein said color-developing agent is imbibed in said photographic element before contact with said amplifier composition.

4. A process according to claim **1** wherein said development restrainer is a benzotriazole compound.

5. A process according to claim **1** wherein said photographic element is developed in an aqueous developer bath comprising a silver halide developing agent before contact with said amplifier composition.

6. A process according to claim **5** wherein said silver halide developing agent is a primary aromatic amino compound.

7. A process according to claim **5** wherein said developer contains at least two silver halide developing agents which comprise a primary aromatic amino compound and at least one other compound which is a black-and-white silver halide developing agent.

8. A process according to claim **5** wherein said silver halide developing agent is a black-and-white silver halide developing agent.

9. A process according to claim **1** wherein said photographic element comprises at least two of said color-providing layer units.

10. A process according to claim **9** wherein each of said color-providing layer units comprises said color coupler in at least a 40 percent stoichiometric excess based on effective silver.

11. In a process of developing an imagewise-exposed photographic element comprising a support and at least one image dye-providing layer unit thereon which contains a light-sensitive silver halide emulsion having associated therewith a color coupler, the improvement comprising development of the imagewise-exposed silver halide emulsion to provide an imagewise distribution of metallic silver and imbibition of a color-developing agent in said photographic element, and then contacting said photographic element with an amplifier composition which contains a development restrainer in a concentration sufficient to repress substantially additional net silver development and wherein said amplifier solution contains a cobalt(III) metal complex having a coordination number of 6 and said amplifier solution is maintained in contact with said photographic element under conditions which reduce said cobalt(III) to cobalt(II) and in turn oxidize said color-developing agent to provide an increase in dye density with dye produced from said coupler in the areas corresponding to the imagewise distribution of said metallic silver.

12. A process according to claim **11** wherein said amplifier bath contains a sufficient quantity of development restrainer to repress substantially any further net silver development.

13. A process according to claim **11** wherein said color-developing agent imbibed in said photographic element is an aromatic primary amino compound.

14. A process according to claim **11** wherein said development of the imagewise-exposed silver halide emulsion is carried out in a liquid which is substantially free of cobalt (III) metal complex salts.

15. A process according to claim **11** wherein said amplifier bath is substantially free of silver halide solvents or contains less than 30 percent by weight of the silver halide solvent which would be necessary to fix a silver halide emulsion.

16. A process according to claim **11** wherein the photographic element is developed in solution and contacted with an amplifying bath which is maintained at temperatures of above 90° F.

17. A process according to claim **11** wherein said color-providing layer unit in said photographic element contains a silver halide emulsion in concentrations of up to 30 mg. of silver per square foot.

18. A process according to claim **11** wherein said photographic element is a multicolor photographic element comprising at least two color-providing layer units which each contains a silver halide emulsion having associated therewith a photographic color coupler in at least a 40 percent stoichiometric excess based on silver.

19. A process according to claim **11** wherein said photographic element is a photographic element comprising at least one image dye-providing layer unit which contains a silver halide emulsion having associated therewith a water-insoluble image dye-providing coupler dissolved in a coupler solvent wherein said coupler is present in at least a 40 percent stoichiometric excess based on effective silver.

20. A process according to claim **18** wherein each of said color-providing layer units contains a silver halide emulsion at a concentration of less than 30 mg. of silver per square foot.

21. A process according to claim **11** wherein the halide concentration of all silver halide emulsions in said element is less than 3 mole persent iodide.

22. A process according to claim **12** wherein said development restrainer is substantially free of ionic iodide groups and free mercapto groups.

23. A process according to claim **12** wherein said development restrainer is the combination of from 0.01 to 2 g./l. of a benzotriazole and from 2 g. to 40 g./l. of an alkali metal bromide.

24. A process according to claim **11** wherein said amplifier bath contains from 2 g. to 40 g. of an alkali metal bromide.

25. A process according to claim **11** wherein said cobalt(III) metal complex is a cobalt hexammine salt.

26. A process according to claim **11** wherein said color-developing agent is 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluenesulfonate.

27. A process according to claim **11** wherein said amplifier bath contains a coupling accelerator which is an alcohol.

28. A process according to claim **11** where development of said silver halide emulsion is carried out in a bath which contains a coupling accelerator which is an alcohol.

29. A process according to claim **11** wherein the halide of the silver halide emulsion in said element is less than 0.25 mole percent iodide.

30. A process according to claim 11 wherein said imagewise-exposed silver halide emulsion is developed in the presence of a black-and-white developing agent.

31. A process according to claim 11 wherein said imagewise-exposed silver halide emulsion is developed in the presence of an aromatic primary amino compound and at least one other compound which is a black-and-white silver halide developing agent.

32. A process for developing an imagewise-exposed photographic element comprising a support having at least one layer unit thereon which contains a silver halide emulsion which has associated therewith at least a 40 percent stoichiometric excess of an image dye-forming color coupler based on silver, which process comprises 1) a development step wherein said photographic element is developed to form an imagewise distribution of silver and an aromatic primary amino color-developing agent is imbibed in said photographic element, and then 2) contacting said photographic element with an amplifier bath containing a) a cobalt (III) metal complex having a coordination number of 6 and b) a development restrainer for sufficient time to produce image dye in addition to any dye produced in said development step.

33. A process for providing or intensifying an image record in an imagewise-exposed photographic element comprising a support having thereon at least one image dye-providing layer unit which contains a light-sensitive silver halide emulsion and a dye image-providing coupler in at least a 40 percent excess based on effective silver, comprising the steps of 1) developing said photographic element in the presence of an aromatic primary amino color-developing agent and 2) contacting said element with an amplifier composition which comprises a cobalt(III) metal complex, an alkali metal bromide at a concentration of from 2 g. to 40 g./l., an organic development restrainer at a concentration of from 0.01 to 2 g./l., and wherein said amplifier composition contains less than 30 percent by weight of the silver halide solvent which would be necessary to fix said silver halide emulsion.

34. A process according to claim 33 wherein the temperature of the amplifier composition is maintained at above 100° F.

35. A process according to claim 33 wherein said cobalt(III) metal complex is cobalt hexammine.

36. A process according to claim 33 wherein said image dye-providing layer unit contains said color coupler in at least a 110 percent stoichiometric excess based on effective silver.

37. A process for providing or intensifying an image record in an imagewise-exposed photographic element comprising a support having thereon at least two image dye-providing layer units each of which contains a light-sensitive silver halide emulsion and at least a 40 percent excess of an image dye-providing color coupler based on effective silver, comprising the steps of 1) developing said photographic element in the presence of an aromatic primary amino color-developing agent and 2) contacting said element with an amplifier composition which comprises a cobalt(III) metal complex, an alkali metal bromide at a concentration of from 2 g. to 40 g./l., an organic development restrainer at a concentration of from 0.01 to 2 g./l., and wherein said amplifier composition contains less than 30 percent by weight of the silver halide solvent which would be necessary to fix said silver halide emulsion.

38. A process according to claim 37 wherein said image dye-providing couplers are water-insoluble couplers dissolved in a coupler solvent.

39. A process according to claim 37 wherein one of said image dye-providing layer units comprises a cyan dye-providing coupler and another of said image dye-providing layer units comprises a magenta dye-providing coupler and each of said layer units comprises said silver halide emulsion at a concentration of less than 30 mg./ft.^{2}.

40. A process according to claim 37 wherein each of said image dye-providing layers contain a 110 percent stoichiometric excess of said image dye-providing color coupler.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,765,891 Dated October 16, 1973

Inventor(s) William Blair Travis

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 2, "fo" should read --for--. Column 7, lines 33-34, "exposue exposure" should read --exposure to--; line 46, "metalic" should read --metallic--. Column 8, line 6, "inert" should read --"inert"--. Column 9, line 37, that part of formula reading "P-" should read -- p- --. Column 13, line 33, that part of formula reading "ditert" should read -- di-tert --; line 46, under the word "stabilize", --dry-- should be inserted; line 55, after "Na_4EDTA", --*-- should be inserted. Column 16, lines 54-55, "apprently apparently" should read --apparently carried--. Column 18, line 12, that part of formula reading "]α" should read --[α--. Column 20, line 43, "persent" should read --percent--; line 62, "where" should read --wherein--. Column 22, line 38, "contain" should read --contains--.

Signed and sealed this 24th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents